Geological Survey of Canada
Commission géologique du Canada

PAPER 87-27

A PROCEDURE TO LOWER THE LIMITS OF DETECTION FOR SILVER, CADMIUM AND LEAD IN THE ANALYSIS OF GEOLOGICAL MATERIALS BY ATOMIC ABSORPTION SPECTROMETRY

G.E.M. Hall
J.L. Bouvier

1988

Canada

88-03059/

GEOLOGICAL SURVEY OF CANADA
PAPER 87-27

A PROCEDURE TO LOWER THE LIMITS OF DETECTION FOR SILVER, CADMIUM AND LEAD IN THE ANALYSIS OF GEOLOGICAL MATERIALS BY ATOMIC ABSORPTION SPECTROMETRY

G.E.M. Hall
J.L. Bouvier

1988

©Minister of Supply and Services Canada 1988

Available in Canada through

authorized bookstore agents and other bookstores

or by mail from

Canadian Government Publishing Centre
Supply and Services Canada
Ottawa, Canada K1A 0S9

and from

Geological Survey of Canada offices:

601 Booth Street
Ottawa, Canada K1A 0E8

3303-3rd Street N.W.,
Calgary, Alberta T2L 2A7

A deposit copy of this publication is also available for reference in public libraries across Canada

Cat. No. M44-87/27E Canada: $4.00
ISBN 0-660-53843-1 Other countries: $4.80

Price subject to change without notice

Critical readers
G.R. Lachance
J.J. Lynch

Original manuscript received: 1987-06-08
Final version approved for publication: 1987-06-24

Contents

1 Abstract/Résumé

1 Introduction

2 Experimental
2 Reagents
2 Instrumentation
2 Procedure

2 Results and discussion

5 Conclusions

5 Acknowledgements

5 References

Tables

3 1. Equivalent concentrations of calibration standards used in the analysis by solvent extraction

3 2. Analysis of the aqueous phase vs. analysis of the solvent-extracted phase in 7 reference materials for Ag.

3 3. Analysis of the aqueous phase vs. analysis of the solvent-extracted phase in 10 reference materials for Cd.

3 4. Analysis of the aqueous phase vs. analysis of the solvent-extracted phase in 11 reference materials for Pb.

4 5. Results of analysis by the proposed procedure of standard reference materials.

A PROCEDURE TO LOWER THE LIMITS OF DETECTION FOR SILVER, CADMIUM AND LEAD IN THE ANALYSIS OF GEOLOGICAL MATERIALS BY ATOMIC ABSORPTION SPECTOMETRY

Abstract

The current method by which geological materials are analyzed for silver, cadmium and lead on a large scale at the Geological Survey of Canada is based upon their determination by atomic absorption spectrometry after a "total" decomposition procedure producing a digestate which is also used for the determination of a suite of other trace elements by ICP-emission spectrometry. Presented here is an efficient and reliable preconcentration method employing extraction of Ag, Cd and Pb as their iodide complexes into an organic medium (Aliquat 336/IBMK) from the same digestate. The extraction significantly lowers the detection levels of these metals; such improvement is demonstrated by application of the procedure to the analysis of international reference materials. The limits of determination are: 0.3μg g^{-1} for Ag; 0.2μg g^{-1} for Cd; and 3 μg g^{-1} for Pb.

Résumé

La méthode actuellement utilisée à la Commission géologique du Canada pour doser l'argent, le cadmium et le plomb dans de nombreux échantillons géologiques fait appel à la spectrométrie d'absorption atomique après une décomposition « totale »; on obtient ainsi un digesté dans lequel on dose également une série d'éléments en traces par spectrométrie d'émission en plasma à couplage inductif. Dans la présente communication, on présente une méthode efficace et fiable de préconcentration comportant l'extraction sous forme de complexes iodés dans un solvant organique (Aliquat 336/IBMK) de l'Ag, du Cd et du Pb contenus dans ce même digesté. L'extraction permet d'abaisser considérablement la limite de détection de ces matériaux; cet avantage est illustré par l'application de cette méthode à l'analyse de matériaux de référence diffusés à l'échelle internationale. Voici les limites de détection de cette méthode : 0,3 μg.g^{-1} pour l'Ag, 0,2 μg.g^{-1} pour le Cd et 3 μg.g^{-1} pour le Pb.

INTRODUCTION

Silver, cadmium and lead are determined routinely at the Geological Survey of Canada by atomic absorption spectrometry (AAS) following a "total" decomposition of the sample with an oxidizing acid mixture ($HF/HClO_4/HNO_3/HCl$) and fusion of any residue with lithium metaborate, $LiBO_2$. The solution thus generated is analyzed by inductively coupled plasma — emission spectrometry (ICP-ES) for a suite of trace elements with the exceptions of the 3 metals under discussion, since their measurement by AAS affords greater sensitivity. However, the dilution factor of 100 produced by the digestion scheme creates inadequate limits of detection for these elements in certain geochemical studies. These determination limits are: 5 μg g^{-1} for Ag; 3 μg g^{-1} for Cd; and 20 μg g^{-1} for Pb. Thus, an investigation was initiated to design a procedure to improve the detection levels while still using the digestate which yields reliable and reproducible results when applied to a wide variety of geological matrices.

Solvent extraction, as a method of preconcentration, was particularly appealing due to the enhanced nebulization efficiency of organic solvents compared to aqueous solutions (Kirkbright and Sargent, 1974). Extraction of the analytes as their iodide complexes into an organic solvent containing Aliquat 336 (tricaprylyl methyl ammonium chloride) in IBMK (isobutyl methyl ketone) was chosen because it is rapid and effective, and separation from major elements, especially Fe, is efficiently achieved without the additional step of backwashing (Clark and Viets, 1981). The presence of excess ascorbic acid and iodide in the aqueous phase reduces Fe to the +2 valency state which does not extract into the organic phase. Sodium, K, Mg, Ca, Al and Si also do not extract into this medium.

The effectiveness of the extraction procedure to improve detection levels for Ag, Cd, and Pb was studied by analyzing both the aqueous phase and IBMK phase of

digested international reference materials. Accuracy was also tested by application of the methodology to these materials.

EXPERIMENTAL

Reagents

All chemicals used were of analytical reagent grade. The aqueous reagent solutions were prepared with distilled, deionised water. Standards were prepared by serial dilution from stock solutions with hydrochloric acid; the presence of nitrate ions was avoided as they deactivate the exchange sites on Aliquat 336. Tricaprylyl methyl ammonium chloride, the quaternary amine known as Aliquat 336, was obtained from General Mills Chemical Division, Minneapolis, MN, U.S.A.

Instrumentation

A Perkin-Elmer 3030 atomic absorption spectrophotometer, equipped with background correction and conventional hollow-cathode lamps, was used for all measurements. A single slot 10 cm burner was employed to support an air-acetylene flame. The wavelengths monitored for the analytes were as follows: Ag, 328.1 nm; Cd, 228.8 nm; and Pb, 217.0 nm. Parameters such as flame conditions and burner position were optimized using analyte standards in both aqueous and organic solvent media.

Procedure

The sample decomposition procedure has been described in detail previously (Hall *et al.*, 1987) and is that used routinely at the Geological Survey of Canada to determine trace elements in various geological media by ICP-ES. Briefly, a 1000 mg sample is digested with the acids, HF, HCl, HNO_3 and $HClO_4$; any residue remaining is rendered soluble by fusion with 0.5 g $LiBO_2$. Nitric acid is removed by evaporation with $HClO_4$; its presence would otherwise inhibit the later extraction of the anlytes as their iodide complexes. The digestate is made up to a final volume of 100 mL and is 1.2 M in HCl concentration.

To a 20.0 mL aliquot of this sample solution in a separatory funnel, 8 mL of 12 M HCl are added, together with 4 mL of an aqueous solution containing the reducing agent, 30% m/V ascorbic acid, and 15% m/V KI. The flask is well shaken and allowed to stand for 30 min. A 6.0 mL aliquot of a solution containing 10% V/V Aliquot 336 in IBMK is added and shaken for 5 minutes on a mechanical oscillator. The organic phase is separated off and analyzed by AAS for Ag, Cd and Pb.

Calibration standards are made by adding appropriate amounts of stock solutions (μL quantities) to 20.0 mL volumes of "blank" 1.2 M HCl, derived from the decomposition procedure, and treated in an identical manner to the unknown sample solutions.

Shown in Table 1 are the concentrations of the mixed standards used for calibration, calculated as equivalent to a sample taken through the extraction described earlier. Absorbance vs. concentration plots show a straight line relationship for all 3 analytes, so a total of 3 standards should suffice for routine applications. If unknown samples contain greater than 20 $\mu g\ g^{-1}$ Ag and Cd or 200 $\mu g\ g^{-1}$ Pb, the extracted solutions would be diluted with 10% Aliquat 336 in IBMK or the aqueous solutions in 1.2 M HCl would be analyzed directly, using similar standards. The solution employed for washing between samples during analysis is 10% Aliquat 336 in IBMK, equilibrated previously by shaking with 3.6 M HCl.

RESULTS AND DISCUSSION

The extraction efficiency for all 3 analytes was in the range 98-100% at the HCl concentration used (3.8 M) in the aqueous phase, in agreement with Viets *et al.* (1984) and O'Leary and Viets (1986). For 2 samples, stream sediments GSD-5 and GSD-7, an emulsion appeared to form immediately upon shaking. However, after allowing the organic layer to settle, this did not interfere with the analysis and results obtained by direct calibration were verified by the method of standard additions. Difficulties reported by Viets *et al.* (1984), where precipitation of Pb and Ag iodides would occur, were not encountered in this work due to low concentrations of the analytes; for high levels, the metals are best determined by analysis of the aqueous phase.

In order to demonstrate the increased sensitivity and improved precision obtained by analyte preconcentration (factor of 3.3) and enhanced nebulization efficiency of an organic solvent, various geological reference materials were analyzed both in the aqueous phase (1.2 M HCl) and in the IMBK phase after solvent extraction. These data are shown in Tables 2, 3 and 4 for Ag, Cd and Pb, respectively. The samples designated LKSD, STSD and TILL belong to a suite of 12 reference materials soon to be released as geochemical reference samples by the Geological Survey of Canada (J.L. Lynch, pers. comm., 1987); the others have been well documented (Govindaraju, 1984). Both phases of each sample were derived from the same decomposition and, within analytical error, the mean values agree well for all 3 elements. The precision of measurement, however, is far superior for the organic phase, generally by ten-fold, and more at the lower levels. Comparison of aqueous and organic solvent calibration standards indicates an improvement in sensitivity by a factor of 10 to 15.

Five 20 mL aliquots of a blank solution representative of the reagents used in the sample decomposition procedure, were carried through the extraction process and analyzed. The equivalent analyte concentrations of these blank solutions and their standard deviations are as follows: Ag, $0.046 \pm 0.035\ \mu g\ g^{-1}$; Cd $0.046 \pm 0.021\ \mu g\ g^{-1}$; and Pb, $0.52 \pm 0.31\ \mu g\ g^{-1}$. Thus, the detection limits, defined as 3 times the standard deviation of the blank, are 0.10 $\mu g\ g^{-1}$ Ag, 0.06 $\mu g\ g^{-1}$ Cd, and 0.9 $\mu g\ g^{-1}$ Pb. However, a more realistic lower limit which would take into account variabilities introduced in the decomposition

Table 1. Equivalent concentrations of calibration standards used in the analysis by solvent extraction atomic absorption spectrometry.

Standard	$\mu g\ g^{-1}$		
	Ag	Cd	Pb
0	0	0	0
1	0.5	0.5	10
2	1.0	1.0	25
3	2.5	2.5	50
4	3.3	3.3	75
5	10	10	100
6	20	20	200

Table 2. Analysis of the aqueous phase vs. analysis of the solvent-extracted phase in 7 reference materials for Ag.

Sample	$Ag/\mu g\ g^{-1}$	
	1.2 M HCl phase mean ± SD	IBMK phase mean ± SD
GXR-2 (soil)	17.3 ± 1.4	16.92 ± 0.10
GXR-4 (copper millhead)	3.1 ± 0.3	3.01 ± 0.02
GXR-5 (soil)	0.6 ± 0.3	0.71 ± 0.02
LKSD-2 (lake sediment)	0.6 ± 0.3	0.71 ± 0.03
LKSD-3 (lake sediment)	2.3 ± 0.6	2.52 ± 0.04
STSD-2 (stream sediment)	0.5 ± 0.4	0.53 ± 0.02
TILL-3 (till)	1.3 ± 0.6	1.51 ± 0.06

SD: Standard deviation based on 5 measurements of 1 s duration.

Table 3. Analysis of the aqueous phase vs. analysis of the solvent-extracted phase in 10 reference materials for Cd.

Sample	$Cd/\mu g\ g^{-1}$	
	1.2 M HCl phase mean ± SD	IBMK phase mean ± SD
BCSS-1 (marine sediment)	0.2 ± 0.4	0.25 ± 0.01
MESS-1 (marine sediment)	0.5 ± 0.4	0.65 ± 0.01
SO-4 (soil)	0.2 ± 0.2	0.44 ± 0.02
GXR-2 (soil)	3.4 ± 0.3	3.81 ± 0.03
GXR-4 (copper millhead)	0.2 ± 0.4	0.30 ± 0.01
MA-N (granite)	1.8 ± 0.2	1.92 ± 0.02
GSD-6 (lake sediment)	0.3 ± 0.3	0.40 ± 0.01
LKSD-2 (lake sediment)	0.6 ± 0.4	0.71 ± 0.01
LKSD-3 (lake sediment)	0.5 ± 0.4	0.60 ± 0.01
STSD-2 (stream sediment)	0.6 ± 0.4	0.68 ± 0.01

SD: Standard deviation based on 5 measurements of 1 s duration.

Table 4. Analysis of the aqueous phase vs. analysis of the solvent-extracted phase in 11 reference materials for Pb.

Sample	$Pb/\mu g\ g^{-1}$	
	1.2 M HCl phase mean ± SD	IBMK phase mean ± SD
BCSS-1 (marine sediment)	22 ± 2	23.1 ± 0.2
MESS-1 (marine sediment)	32 ± 1	34.2 ± 0.5
SO-4 (soil)	16 ± 3	16.1 ± 0.2
GXR-4 (copper millhead)	46 ± 4	46.9 ± 0.6
GXR-5 (soil)	14 ± 6	15.3 ± 0.4
GSD-6 (stream sediment)	29 ± 3	30.5 ± 0.3
GSD-8 (stream sediment)	23 ± 2	20.8 ± 0.1
MA-N (granite)	29 ± 2	31.2 ± 0.2
LKSD-2 (lake sediment)	47 ± 4	47.4 ± 0.3
LKSD-3 (lake sediment)	33 ± 3	32.8 ± 0.4
STSD-2 (stream sediment)	71 ± 3	73.2 ± 0.5

SD: Standard deviation based on 5 measurements of 1 s duration.

Table 5. Results of analyses by the proposed procedure of standard reference materials; 3 extractions performed per decomposition.

Concentrations in $\mu g\ g^{-1}$.

Sample	Ag		Cd		Pb	
	This method	Literature value	This method	Literature value	This method	Literature value
BCSS-1 (marine sediment)	<0.3		0.27 ± 0.04	0.25[a]	23 ± 1	22.7[a]
MESS-1 (marine sediment)	<0.3		0.67 ± 0.05	0.59[a]	35 ± 2	34[a]
SO-4 (A-horizon soil)	<0.3	<2[b]	0.46 ± 0.11	0.34 ± 0.07[b]	16 ± 1	14 ± 5[b]
GXR-2 (soil)	17.4 ± 0.7	18 ± 3[c]	3.8 ± 0.1	4.1 ± 0.4[c]	>500	670 ± 50[c]
GXR-4 (copper millhead)	3.2 ± 0.11	3.2 ± 0.8[c]	0.32 ± 0.06	0.52 ± 0.22[c]	48 ± 3	47 ± 4[c]
GXR-5 (B-horizon soil)	0.63 ± 0.22	0.93 ± 0.25[c]	<0.2	0.20 ± 0.07[c]	17 ± 2	15.6 ± 1.6[c]
GSD-5 (stream sediment)	0.30 ± 0.08	0.36 ± 0.04[d]	0.81 ± 0.07	0.82 ± 0.07[d]	116 ± 1	112 ± 13[d]
GSD-6 (stream sediment)	<0.3	0.36 ± 0.04[d]	0.45 ± 0.09	0.43 ± 0.04[d]	30 ± 1	27 ± 5[d]
GSD-7 (stream sediment)	1.1 ± 0.1	1.05 ± 0.09[d]	1.1 ± 0.1	1.05 ± 0.08[d]	351 ± 5	350 ± 26[d]
MA-N (granite)	0.89 ± 0.19	2[a]	2.0 ± 0.1	2[a]	31 ± 1	29[a]
LKSD-2 (lake sediment)	0.69 ± 0.08	0.8[e]	0.74 ± 0.14	0.6[e]	48 ± 1	44[e]
LKSD-2 (separate decomposition)	0.63 ± 0.08		0.72 ± 0.06		47 ± 1	
LKSD-3 (lake sediment)	2.5 ± 0.2	2.7[e]	0.58 ± 0.07	<0.5[e]	32 ± 1	30[e]
LKSD-3 (separate decomposition)	2.5 ± 0.2		0.48 ± 0.12		33 ± 1	
STSD-2 (stream sediment)	0.48 ± 0.09	0.5[e]	0.65 ± 0.07	0.6[e]	74 ± 1	66[e]
STSD-2 (separate decomposition)	0.49 ± 0.07		0.61 ± 0.05		75 ± 1	
TILL-3 (till)	1.4 ± 0.2	1.6[e]	<0.2	<0.5[e]	19 ± 1	18[e]
FeR-2 (iron-formation)	<0.3	0.2[f]	<0.2	0.35,6.1[f]	8 ± 1	6–15[f]
FeR-3 (iron-formation)	<0.3	0.3[f]	<0.2	0.27,6.8[f]	5 ± 1	5–13[f]
FeR-4 (iron-formation)	<0.3		<0.2	0.20,6.1[f]	5 ± 1	7–16[f]

a Govindaraju, (1984)
b Gladney *et al.*, (1985)
c Gladney *et al.*, (1984)
d Xuejing *et al.*, (1985)
e Lynch (pers. comm., 1987)
f Abbey *et al.*, (1983)

itself is thought to be about 3 times this figure. Hence, the suggested determination limits are 0.3 $\mu g\ g^{-1}$ for Ag, 0.2 $\mu g\ g^{-1}$ for Cd and 3 $\mu g\ g^{-1}$ for Pb by this procedure. Care must be taken when changing to different lot numbers of acids or reagents such as KI, because we have found significant changes to 'blank' levels, particularly for Pb.

Seventeen reference materials were decomposed and each solution analyzed in triplicate by the proposed procedure. The results, together with literature values, are given in Table 5. The FeR series of rocks which contain Fe in the range 39-44% Fe_2O_3 were also analyzed by the method of standard additions for each element and the values agreed with those obtained by direct calibration, indicating that the quantity of ascorbic acid used was sufficient to reduce Fe to the +2 state and thereby prevent its extraction. Cadmium and Pb could not be determined previously in the aqueous phases of the iron-formation samples due to the presence of such high Fe concentrations which caused a negative error in the AAS measurement, as has also been reported by Clark and Viets (1981). Thus, the solvent extraction procedure has not only improved detection levels but has also made possible the analysis of such troublesome matrices for Cd and Pb.

There is good agreement between the results obtained by this procedure and the compiled values available from the literature for the international series such as the GXR and GSD samples. The values for the GXR series agree well with those reported by O'Leary and Viets (1986); for example, Cd in GXR-2 (3.8 $\mu g\ g^{-1}$ vs. 3.85 $\mu g\ g^{-1}$), Cd in GXR-4 (0.32 $\mu g\ g^{-1}$ vs. 0.38 $\mu g\ g^{-1}$) and Ag in GXR-5 (0.63 $\mu g\ g^{-1}$ vs. 0.72 $\mu g\ g^{-1}$), and these values are somewhat lower than the 'literature values' for these samples reported by Gladney *et al.*, (1984). There are few literature values for the Ag content of the granite MA-N, and this may explain the discrepancy between our value of 0.89 $\mu g\ g^{-1}$ and the 2 $\mu g\ g^{-1}$ quoted in Table 5 which is a proposed rather than recommended value. The precision indicated by the standard deviation shown for each mean result reflects only the variability due to the extraction and analysis, not to the digestion procedure. An appreciation of the precision of the entire decomposition, extraction and analysis can be gained by examining the data for samples LKSD-2, LKSD-3 and STSD-2 which were decomposed in duplicate. The quality in precision evidenced here is also seen in the analysis carried out by ICP-ES for other trace elements for which this decomposition was designed (G.R. Lachance, pers. comm., 1987). Judgement of the accuracy of these data cannot be made at this time because of the limited number of analyses for these elements, particularly Ag, and the values cited for reference in Table 5 are "probable" rather than "proposed". This also applies to the FeR series of rocks where comparatively few results have been published; these samples were included to demonstrate the ability of the procedure to effectively analyse otherwise problematic matrices.

CONCLUSIONS

A rapid, efficient and precise method has been designed and tested by which the detection limits for Ag, Cd and Pb in geological materials can be improved approximately by ten-fold, while still using the digestate suitable for other multi-element determinations. The method is applicable to samples containing the elements in the concentration ranges 0.3 - 20 $\mu g\ g^{-1}$ Ag, 0.2 - 20 $\mu g\ g^{-1}$ Cd and 3 - 200 $\mu g\ g^{-1}$ Pb. Once the samples have been decomposed, it is estimated that 80 per day could be extracted and analyzed for all 3 elements. This productivity will increase dramatically when the extraction procedure becomes automated by flow injection, a project currently under investigation.

ACKNOWLEDGMENTS

The authors wish to thank J.J. Lynch and G.R. Lachance for their contributions to this project.

REFERENCES

Abbey, S., McLeod, C.R., and Liang-guo, W.
1983: FeR-1, FeR-2, FeR-3 and FeR-4, Four Canadian iron-formation samples prepared for use as reference materials; Geological Survey of Canada, Paper 83-19, 51 p.

Clark, J.R. and Viets, J.G.
1981: Multielement extraction system for the determination of 18 trace elements in geochemical samples; Analytical Chemistry, v. 53, p. 61-65.

Gladney, E.S., Burns, C.E., and Roelandts, I.
1984: 1982 compilation of elemental concentration data for the United States Geological Survey's geochemical exploration reference samples GXR-1 to GXR-6; Geostandards Newsletter, v. VIII, p. 119-154.
1985: 1983 compilation of elemental concentration data for samples SO-1 to SO-4; Geostandards Newsletter, v. IX, p. 35-68.

Govindaraju, K.
1984: 1984 compilation of working values and sample description for 170 international reference samples of mainly silicate rocks and minerals; Geostandards Newsletter, v. VIII, p. 3-85.

Hall, G.E.M., DeSilva, K.N., Pelchat, J.C., and Vaive, J.E.
1987: Advances in analytical methods based on atomic absorption spectrometry in the Geochemistry Laboratories of the Geological Survey of Canada; *in* Current Research, Part A, Geological Survey of Canada, Paper 87-1A, p. 477-484.

Kirkbright, G.F. and Sargent, M.
1974: Atomic absorption and fluorescence spectroscopy; Academic Press Inc., London, 331 p.

O'Leary, R.M. and Viets, J.G.
1986: Determination of antimony, arsenic, bismuth, cadmium, copper, lead, molybdenum, silver, and zinc in geological materials by atomic absorption spectrometry using a hydrochloric acid — hydrogen peroxide digestion; Atomic Spectroscopy, v. 7, p. 4-8.

Viets, J.G., O'Leary, R.M. and Clark, J.R.
1984: Determination of arsenic, antimony, bismuth, cadmium, copper, lead, molybdenum, silver and zinc in geological materials by atomic absorption spectrometry; Analyst, v. 109, p. 1589-1592.

Xuejing, X., Mingcai, Y., Lianzhoug, L., and Huijun S.
1985: Geochemical reference samples drainage sediment GSD 1-8 from China; Geostandards Newsletter, v. IX, p. 83-160.

Energy, Mines and Resources Canada

Énergie, Mines et Ressources Canada